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ON RAINBOW SCATTERING IN INELASTIC MOLECULAR COLLISIONS

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The purpose of this letter is to call attention to a growing misinterpretation in the literature on rainbow scattering in inelastic molecular collisions. The importance of rainbow structures in the angular distributions of elastic scattering cross sections is well established.¹ A few years ago it was suggested that similar structure may also be experimentally observable in the distribution of inelastic scattering cross sections vs. the discrete final molecular rotational angular momentum.² Since then a number of experiments³⁻⁵ have clearly demonstrated the existence of such structure, and the work of Schepper et al^{4,6} leaves little doubt that the rainbow explanation of it is correct. Several recent experiments have also reported rainbow structures in the angular distributions of rotationally inelastic cross sections.⁷⁻¹⁰ The importance of these developments lies in the possibility that with sufficient theoretical development and experimental resolution, they may lead to direct experimental measurement of certain anisotropic features in the intermolecular potential energy surfaces.

However, the work of Schinke¹¹ and Bowman,¹² using approximate cross section formulas has led to an incorrect classification of the types of rainbows which are possible. Using a stationary phase approximation to an already-approximate (IOS) quantum mechanical theory, they arrive at cross section formulas for the scattering of a structureless particle from a linear rigid rotor, which predict separate rainbow singularities when the derivatives $\left. \frac{\partial j}{\partial \gamma} \right|_b$ and $\left. \frac{\partial \theta}{\partial b} \right|_\gamma$ are, respectively, zero. Here j is the final rotational angular momentum of the rotor, θ is the deflection angle, b is the initial impact parameter and γ is the rotor's initial angle of orientation. Bowman errs when he claims that zeros of these two derivatives predict the locations of the classical rainbows. The classical expression for the cross section in this case^{2,13} contains a Jacobian determinant of derivatives and the rainbows are located at zeros of

$$\frac{\partial(j, \theta)}{\partial(b, \gamma)} = \left. \frac{\partial j}{\partial b} \right|_\gamma \left. \frac{\partial \theta}{\partial \gamma} \right|_b - \left. \frac{\partial j}{\partial \gamma} \right|_b \left. \frac{\partial \theta}{\partial b} \right|_\gamma \quad . \quad (1)$$

Unless one can show that the pair of derivatives $\left(\left. \frac{\partial j}{\partial \gamma} \right|_b, \left. \frac{\partial \theta}{\partial \gamma} \right|_b \right)$ are simultaneously zero and likewise for the other pair, it is not possible to classify the singularities as "impact parameter" or "orientation angle" types. In fact, it is easily demonstrated by running a few trajectories on almost any anisotropic potential energy surface, including purely repulsive ones, that the derivatives $\left. \frac{\partial j}{\partial \gamma} \right|_b$ and $\left. \frac{\partial \theta}{\partial \gamma} \right|_b$ are not, in general, simultaneously zero.

Actually, however, it is possible to identify two classes of rainbows. If we consider the final, rather than the initial trajectory

values as independent variables, then the rainbows will occur at the infinities of the Jacobian,

$$\frac{\partial(b,\gamma)}{\partial(j,\theta)} = \frac{\partial b}{\partial j}\bigg|_{\theta} \frac{\partial \gamma}{\partial \theta}\bigg|_j - \frac{\partial b}{\partial \theta}\bigg|_j \frac{\partial \gamma}{\partial j}\bigg|_{\theta} . \quad (2)$$

In this case it is possible to show under rather general conditions that the pair of derivatives $(\frac{\partial b}{\partial j}\big|_{\theta}, \frac{\partial \gamma}{\partial j}\big|_{\theta})$ are simultaneously infinite and likewise for the other pair. Therefore it is possible to classify the rainbows according to derivatives with respect to the final trajectory variables, θ and j . This is apparent from purely geometrical considerations and was stated without proof in Ref. 2. A detailed discussion of these points, illustrated with specific examples, will be given in a future publication.¹⁴

Similarly, it is worthwhile to call attention to the growing number of names being used to describe these structures. The terms rotational rainbow, angular rotational rainbow, bulge singularity, and halo have all been used — ambiguously in some cases. The common feature is the structure in the cross section due to a singular Jacobian in the classical formula. To be completely unambiguous, one should specify in which distribution the structure is observed — angular, rotational, etc. — and, in cases where the identification can be made, classify the structure according to the final trajectory variable, derivatives with respect to which are responsible for the classical singularity: θ , j , etc. Many naming conventions are possible and differing personal preferences will undoubtedly lead to a continuing variety of names in the literature. If the relevant distributions and classifications are clearly stated, there should be little chance of confusion. However, the term "halo"¹⁰

seems inappropriate since the analogy is based on an incorrect location of the classical singularity.

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